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Preventing Cracking of Anodized Coatings

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ABSTRACT

Anodized coatings have been used as optical and thermal surfaces in spacecraft. Particulate contamination from cracked coatings is a concern for many applications. The major cause for the cracking is the difference in the coefficient of thermal expansion between the oxide coatings and the aluminum substrate. The loss of water when the coating is exposed to a vacuum also could induce cracking of the coating. Hot-water sealing was identified as the major cause for the cracking of the coatings because of the large temperature change when the parts were immersed in boiling water and the water was absorbed in the coating. When the hot-water sealing process was eliminated, the cracking resistance of the anodized coatings was greatly improved. Also it was found that dyed black coatings were more susceptible than clear coatings to cracking during thermovacuum cycling.

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I. INTRODUCTION

Anodizing is a surface-treating process that creates a hard, corrosion- and abrasion-resistant oxide coating on aluminum alloys. These properties, combined with superior adhesion and dielectric strength of the anodized coating, allow aluminum to be substituted for costlier materials in many applications. Clear anodic oxide coatings have high emissivity and low absorptivity that result in efficient radiative heat transfer, and the coating is stable in the space environment [1]. Black anodized coatings with high emissivity are used in spacecraft to provide reference optical signals for the calibration of instruments. Particulate contamination, however, from crazed coatings is a concern in many applications. In addressing this concern for a NASA project, information concerning the cracking of aluminum anodized coating was developed that may be of general interest.

II. BACKGROUND

In the anodizing process, an electric current is introduced into an electrolytic bath in which the aluminum part has been immersed. The current density and the operating temperature of the bath for conventional anodizing ranges from 90 to 120 A/m² (8 - 11 A/ft²) and from 20° to 25 °C (70°-75 °F), respectively [2]. Increasing current density and lowering operating temperatures usually result in a more dense coating. The variables involved in the process include composition and surface finishing of the aluminum alloy, current density, voltage, temperature of the bath, chemical composition and concentration of the electrolyte, duration of the anodizing process, etc. During the anodizing, aluminum reacts with the electrolyte and a layer of aluminum oxide is formed on the surface of the aluminum specimen. This coating is highly porous and is subject to attack from the environment and corrosive elements. Therefore, anodized aluminum is normally processed with a sealing process as a final step after anodizing. A hot-water sealing process is one of the widely used methods [1]. The specimen is immersed in deionized water at or near the boiling point (100 °C or 212 °F). In this process, the aluminum oxide reacts with water to form aluminum hydroxide, which fills pores in the coating and seals the surface.

The coefficient of thermal expansion of aluminum is about five times greater than that of aluminum oxide [3-5]. As a result, anodized coatings tend to craze or crack mainly because of the thermal stresses. Cracking of the coating may occur during fabrication and/or during operation. Any environmental change that causes differential expansion or shrinking between the coating and the substrate will introduce stresses into the coating. If the stresses are large enough, cracking will occur. The cyclic temperature changes in vacuum in space applications are the potential factors that cause crazing problems. The cracking of the coatings changes the optical and thermal properties of the coating and may cause particulate contamination. Therefore, the crazing of anodized coatings should be avoided in space applications.

Alwitt and his colleagues investigated the thermal stresses in the coating during the anodizing process and under various environments [4,5]. It was found that after anodizing, the stress in the coating was always compressive and independent of coating thickness. The stress was about 16 MPa at 15 V of anodizing voltage and increased with increasing voltage. When the specimen was immersed in boiling water for sealing, the stress became tensile immediately and was large, arising from the greater thermal expansion of the metal than that of the oxide (this could be the moment that crazing of the coating occurs). This stress, however, was greatly reduced as the seal reaction proceeded. At the end of the sealing, the stress in the coating became compressive again. After the coating was dried at ambient temperature, the stress was always compressive. When the coating was exposed in dry air, the stress changed to tensile. The tensile stress in the coating increased with decreasing humidity in the environment. The coating lost weight in dry air, and the weight loss increased with decreasing humidity. It has been proposed that the anodic oxide consists of an array of alumina crystallites [6] with typical dimensions of several nanometers [7]. Interpretations of both infrared (IR) [6] and nuclear magnetic resonance (NMR) [7] spectra lead to the conclusion that the sealed oxide contains both molecular water and water present as hydroxyl groups. Exposed alumina surfaces are presumed to be hydroxylated during sealing, with physisorbed molecular water residing in the intercrystallite space. The weight loss of 1.1% - 3.6% of coating weight can be removed by heating at moderate temperature or under vacuum at room temperature [4,7]. It was also found that the exchange of water with the atmosphere was a reversible process, and the rate of water loss is much slower than the subsequent rate of water recovery [4].

If the crazing does not occur after anodizing and sealing processes, heating the coating can induce the cracking. The temperature at which the cracks first appear on the anodized coatings, T_c , was evaluated by Alwitt and McClung [5]. It was found that there was a general tendency for 25 μm thick coatings to crack at temperatures about 20° to 25 °C lower than for 12.5 μm coatings. This means that thick coatings are more vulnerable to cracking than thin coatings [3,5]. Measurement of tensile failure strain of the oxide scale on the surface of iron also confirmed that thin oxide scale failed at higher strains than thick oxide scale [8]. This means that thin surface layers are more crack resistant than thick surface layers. The reason for this thickness-dependence of crazing is associated with the critical flaw size in the surface layer [8].

In summary, the factors that affect cracking of the anodized coatings are as follows:

1. *Temperature:* Temperature is the most important factor for cracking of anodized coating. The tensile stress in the coating is proportional to the temperature change [6]. Both hot-water sealing and thermal cycling may cause the formation and propagation of cracks.
2. *Humidity of environment:* Low humidity causes loss of water from the coating, which generates large stresses in the coating. Tensile stress and the weight loss of

coatings increase with decreasing humidity [4]. For example, the stress in a typical sealed coating was 20 MPa (3 ksi) compressive in ambient atmosphere at 25 °C. After 2 days in vacuum, the stress was 110 MPa in tension (16 kpsi) [4].

3. *Thickness of the coatings:* Thicker coatings tend to crack at lower temperatures [3,5].
4. *Sealing techniques:* Hot-water sealing can cause the crazing of anodized coatings. The temperature change during hot-water sealing introduces thermal stresses. The water absorbed in the coating during the sealing process escapes into vacuum or low-humidity environments and causes crazing. Some sealing methods, such as low-nickel seal and no-nckel seal, can result in higher crazing resistance of the coating than hot-water sealing method [5].

The purpose of this study is to investigate the feasibility of eliminating the cracking of anodized coatings by eliminating the hot-water sealing process. The purpose of hot-water sealing is to seal the porous coatings to protect the substrate from attack by environment. In the space environment, however, there are little moisture and other chemicals that attack the coatings. Corrosion is not a major concern for space applications of the anodized coatings.

III. EXPERIMENT

Four anodized plates (76 x 76 x 1.5 mm, or 3 x 3 x 1/16") of Aluminum 1100 with different coating thicknesses were obtained from the Goddard Space Flight Center Plating Shop (specimens B to E, Table 1). The anodizing was performed in a 15 vol% H₂SO₄ solution at 68°F. Those specimens were not hot water sealed. The characteristics of the specimens and the anodized conditions are listed in Table 1.

Table 1. The Characteristics of the Anodized Specimens

Specimen	Coating	Thickness μm (mil)
A	black, sealed	31 (1.5)
B	clear, unsealed	18 (0.7)
C	clear, unsealed	25 (1.0)
D	clear, unsealed	61 (2.4)
E	black, unsealed	31 (1.5)

Small specimens (about 10 x 10 mm, or 3/8" x 3/8") were cut from the received plates. The specimens were cleaned with acetone and dried in air. The specimens were thermocycled in a vacuum furnace. The vacuum was maintained below 10⁻⁶ torr through the test. The temperature was cycled between 25 °C and 115 °C for three

cycles. The dwell time is one hour at 115 °C and overnight at 25 °C. The heating and cooling rates are less than 2 °C/min. The test took a total of about 100 hours during which time the specimens were maintained in vacuum. The surfaces of the coatings were examined using optical microscopy and scanning electron microscopy (SEM) before and after the thermocycling.

IV. RESULTS

Specimen A is a commonly used anodized black coating sealed in hot water. Figure 1 shows the surface of specimen A in the as-received condition. Randomly distributed cracks are observed on the surface. Figure 2 shows the surface of specimen E, which is an unsealed black coating of the same thickness. No cracks are visible. Specimens B through D also do not have any cracks in the as-received condition (prior to thermocycling), although those specimens have varying thickness of from 18 to 61 µm. This suggests that the hot-water sealing could be the major cause for the crazing problem, as inferred from searching the literature.

After thermocycling in vacuum, the specimens were observed again. Figure 3 shows the surface of specimen A. The fine cracks flaked particles from 13 to 50 µm in size. This poses a serious contamination problem for space application. As discussed earlier in this paper, the major causes for this crack enhancement include the thermal stress induced by the temperature changes and the loss of water from the coating caused by the vacuum environment.

For the unsealed clear coatings (specimens B, C, and D), no cracking occurs during the combination of thermocycling and vacuum. Figure 4 shows the surface of specimen B after thermocycling.

For unsealed black coating (specimen E), there are no microcracks observed after thermocycling, as shown in Figure 5. However, several large cracks are observed (Figure 6). Five cracks are observed on a 16 x 22 mm (5/8" x 7/8") area. This is still much better than the sealed black coating (Figure 1a) where small-particulate contamination generated by small sizes of cracks presents a potential danger. The long cracks in the unsealed black coating are unlikely to shed particles and to cause contamination problems.

The above observation suggests that the dyeing process changes the structure and properties of the coating somewhat. Since the black dye is most likely to penetrate into the pores in the coating, the dyeing process may increase the apparent density of the coating. This reduces the effectiveness of stress relaxation by pores and increases the possibility of cracking.

Although the cracking resistance of anodized coatings can be improved by elimination of the sealing process, it may cause other problems. Dye bleeding could occur if the

coating needs to be machined using coolant. Individual circumstances should be taken into account when eliminating the sealing process.

V. CONCLUSION

Hot-water sealing process was identified as a major cause for the cracking of anodized coatings. Elimination of the hot-water sealing greatly improves the cracking resistance of the coatings. Dyed black coatings are more susceptible than clear coatings to the cracking during thermocycling in vacuum.

VI. ACKNOWLEDGMENT

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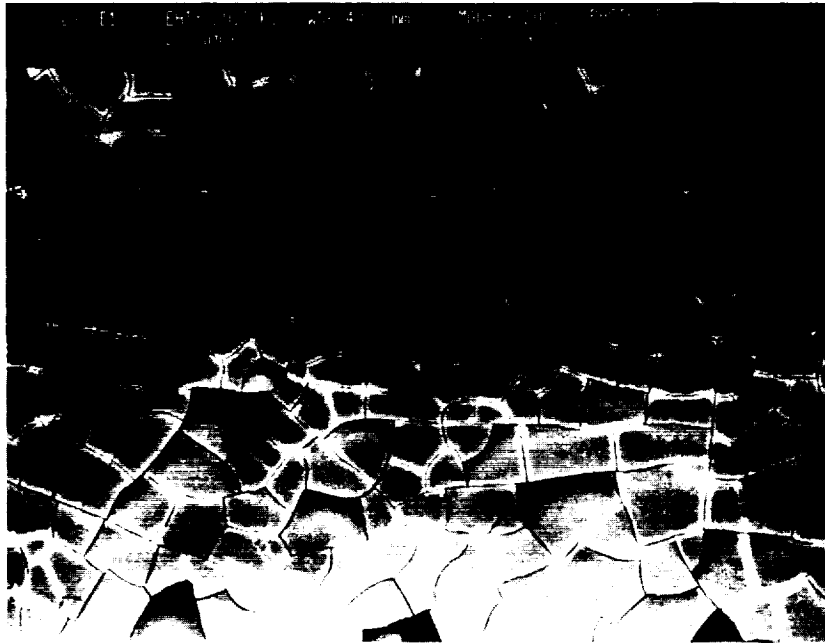


Figure 1. SEM micrograph of Sample A (31 μm or 1.5 mil black anodized coating with hot-water sealing) in as-received condition. The coating cracked severely.

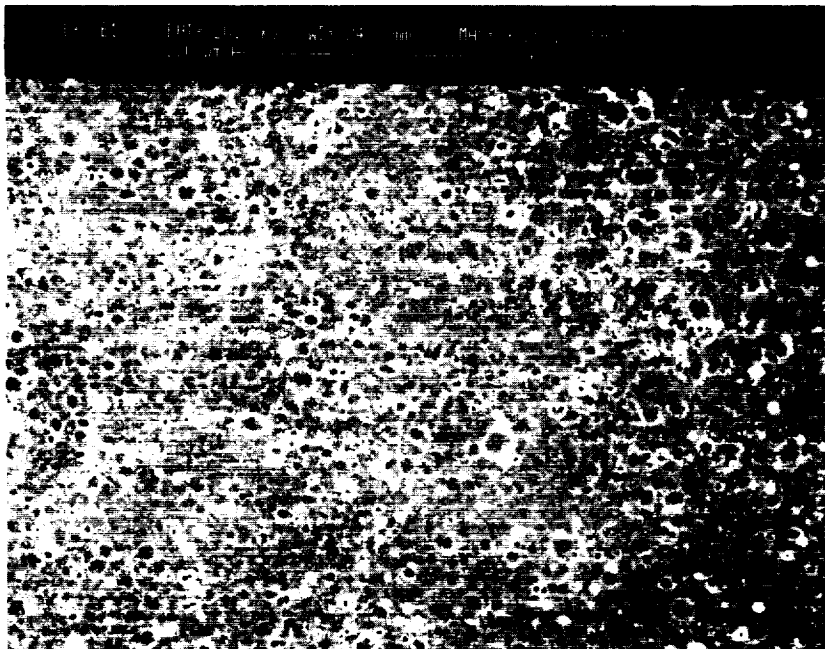


Figure 2. Sample E (31 μm or 1.5 mil black anodized coating without hot-water sealing) in as received condition. No cracks are present.

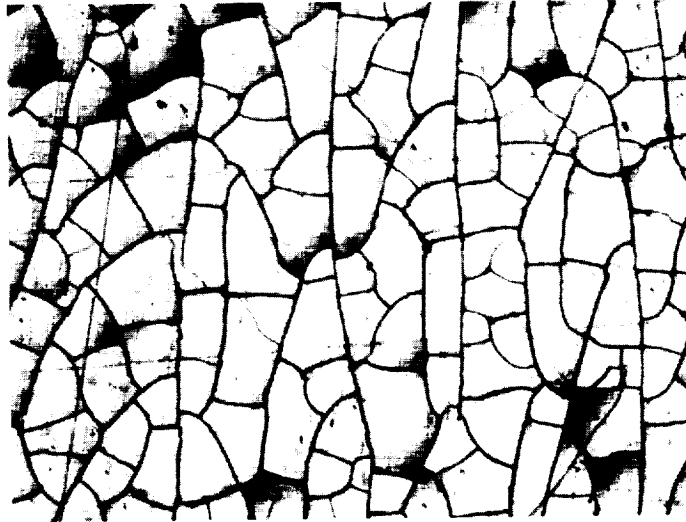


Figure 3. Optical micrograph of Sample A after thermovacuum cycling tests. Magnification is the same as in Figure 1 (200x).

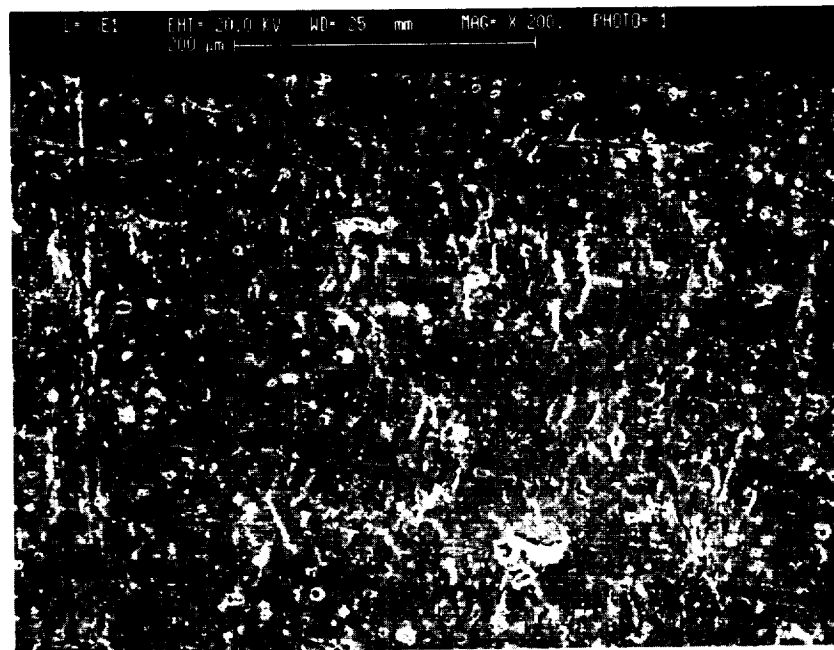


Figure 4. Sample B (18 μm or 0.7 mil clear coating without hot-water sealing) after thermovacuum cycling test. No cracks are observed.

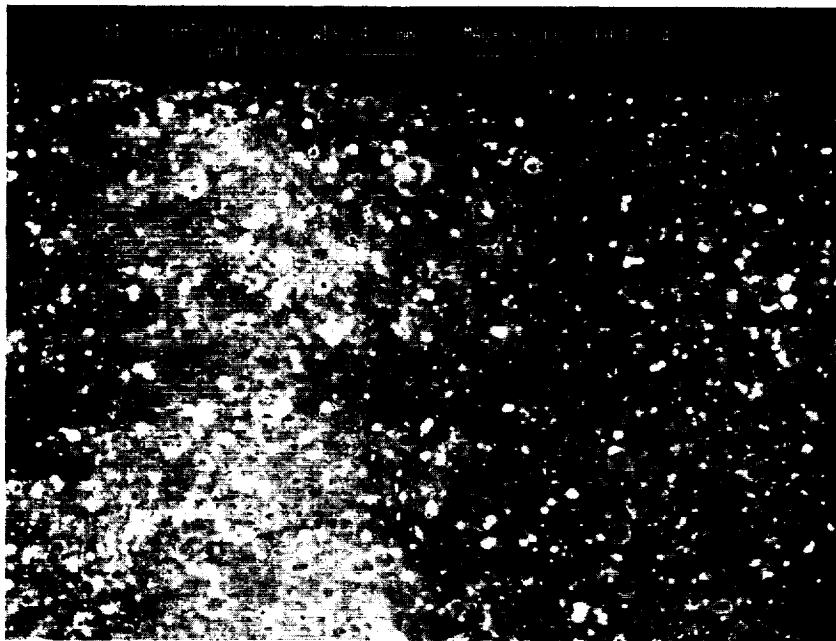


Figure 5. Sample E (31 μm or 1.5 mil black coating without hot-water sealing) after thermovacuum cycling test. There are no small cracks as observed in Figures 1 and 3.



Figure 6. Sample E after thermocycling. Several large cracks are present. These large cracks should not cause any particulate contamination.

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